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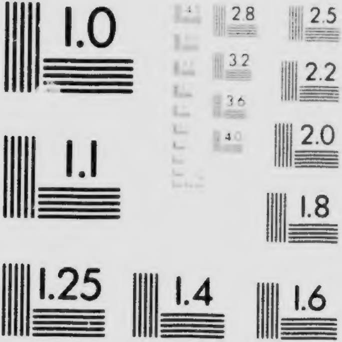

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By

J. B. TYRRELL, F.R.S.C., and R. P. D. GRAHAM.

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Yukonite, a New Hydrous Arsenate of Iron and Calcium, from Tagish Lake, Yukon Territory, Canada; with a note on the Associated Symplesite.

By J. B. Tyrrell, F.R.S.C., and R. P. D. Graham.

Mode of Occurrence. By J. B. Tyrrell.

The mineral here called Yukonite was found by the writer in the autumn of 1906 on a mining claim on the west side of Windy Arm of Tagish lake, in the southern portion of the Yukon Territory, Canada. The claim was just south of the "Venus" and at the time was being operated by Mr. T. M. Daulton.

The country in which the mineral occurs is a part of the Coast or Chilcat range of mountains, which rises in peaks and ridges to heights of seven or eight thousand feet above the sea. It is crossed by many transverse valleys in which often lie deep, clear, blue lakes, from the sides of which the land rises in slopes which are sometimes precipitous but are more often regularly and evenly graded to the summits. Many of these slopes are covered with a variable thickness of broken and partly decomposed rock which, in the more exposed places, support an Arctic moorland vegetation, while on the sides and in the bottoms of some of the deeper lateral gorges growths of coniferous timber manage to subsist.

Tagish lake, with an elevation of 2160 feet above the sea, occupies the bottom of one of these transverse valleys and discharges its waters into the upper portion of the Yukon river.

It is an irregularly shaped body of water, and its long southern extension, which reaches down into the province of British Columbia, is known as Windy Arm. From the north-west side of this arm, a short distance north of the southern boundary of the Yukon territory, a steep moorland slope rises to a height of several thousand feet, and on this slope, but especially near its base, several quartz veins were discovered carrying silver-bearing galena associated with pyrargyrite, argentite, chalcopyrite, arsenopyrite, and other minerals.

The country rock in which these veins occur is a fine grained greenish porphyrite of Jurassic or Cretaceous age. On account of the severity of the climate, it is perpetually frozen to a considerable, though unknown, depth.

The veins strike north-west and south-east and dip at a high angle into the hill away from the lake. Several of them had been opened by inclined shafts and adits. They were found to show three well-defined zones as follows in descending order: first, a zone of oxidation and leaching; second, a zone of secondary sulphide enrichment; third, a zone of poor, low-grade primary ore.

One of these veins was being opened by Mr. Daulton by a shaft following its dip. The vein matter was quartz, mixed with galena and other sulphides, with considerable loose ochreous material near the surface. A few feet below the surface, and within the zone of oxidation, I found small irregular masses, up to the size of a walnut, of a brown translucent resin-like substance which, on being taken into the warm hand or out into the air, quickly flew into small sharply angular pieces. So readily did the substance break up that it was found quite impossible to carry away clean coherent masses of any considerable size. Those which I did collect and carry away were put into the hands of the late Professor B. J. Harrington of McGill University, Montreal, for determination and description, but his ill health and subsequent death prevented the completion of his examinations. The work was subsequently put into the hands of Professor Graham, and most of the material which remained in my possession has been used by him in making the examinations, the results of which are given below.

Chemical and Physical Properties. By R. P. D. Graham.

The mineral, which is nearly black in colour with a brownish tinge, occurs as irregular concretionary masses embedded in a pale yellowish brown earthy material resembling ochre; the lustre is vitreous inclining to pitchy. As seen in mass, it appears opaque, but fine splinters examined under the microscope transmit light of a deep brown to yellowish brown colour depending on their thickness; they are clear and homogeneous, but isotropic, the substance being amorphous. The hardness is between 2 and 3 and the streak brownish yellow. The mineral is extremely brittle, breaking sharply with a smooth to conchoidal fracture. A remarkable and distinctive property is observed when fragments are immersed in water: these immediately commence to fly to pieces with a crackling sound and the disengagement of gas, very much after the manner of *aquacreptite* which it further resembles in general appearance. This property was first observed during the determination of the specific gravity by the pycnometer method, and owing to this it is impossible to arrive at any exact value for the specific gravity, since the density becomes progressively higher as more and more gas is liberated. In the determination made, the specific gravity was found to be 2.65 immediately after immersion in the water, and it had risen to 2.86 after allowing the bottle to stand for 30 hours.

Even then, gas still continued to be slowly disengaged, but the above figures are sufficient to indicate the order of the specific gravity, and no further determination was made.

In order to determine the nature of these gases, a quantity of the material was heated *in vacuo* and the gas evolved was drawn off and collected over mercury. Quantitative exactness was not aimed at, but a volume of gas was obtained several times as large as that of the substance taken. On examination this proved to be almost entirely carbon dioxide; the volume remaining after absorption by potash solution was too small to be analysed, but it was partly, if not entirely, nitrogen. This carbon dioxide does not appear to be present in the mineral in the form of carbonate, since there is no perceptible effervescence on treatment with hydrochloric acid, even after warming; further, when thin fragments were examined under the microscope with a high power, no cavities such as might enclose liquid carbon dioxide were observed. It would thus seem probable that the gas is held in the imperfectly understood occluded state, and that its ready disengagement from this condition accounts for the shattering which fragments undergo when placed in water, while the extreme brittleness may also be in part due to the same cause. Dr. A. S. Eve, of the McGill University Physics Department kindly examined some of the material for the possible presence of radioactive substances, with negative results.

Clean material for analysis can easily be separated from the earthy yellow matrix. It was found to be easily and completely soluble in hydrochloric acid, with the exception that a little finely divided quartz usually remains undissolved. A qualitative analysis showed the mineral to be a hydrous arsenate of iron and calcium. The method used in the anlaysis was as follows.

The carefully selected material was ground up and dissolved in hydrochloric acid, the solution after dilution being filtered to remove the small amount of quartz which remained undissolved. The solution was then treated with sodium sulphite to reduce the arsenic to the arsenious state, and this was then precipitated by hydrogen sulphide as As_2S_3. In one case the latter was weighed directly after drying at 100° C, but in two other determinations the precipitate was dissolved, and after oxidising with potassium chlorate the arsenic was precipitated by magnesia mixture, filtered through a Gooch crucible and, after igniting, weighed as magnesium pyro-arsenate. The iron and calcium were determined by the usual methods.

An analysis was originally made some years ago on material taken from a small specimen sent to the McGill University Mineral Department by Mr. J. B. Tyrrell for identification. Two separately selected samples gave the following results:—

	1.	2.
CaO	10.00	10.14
Fe_2O_3	35.72	36.81
As_2O_5	34.06	33.83

A more recent analysis made of another specimen since supplied by Mr. Tyrrell yielded results which are essentially similar, though the As_2O_5 was higher and the Fe_2O_3 lower than in the above. The differences observed are no doubt due to small amounts of foreign admixtures in the samples taken—either of the yellow ochreous material in which the mineral is embedded, or of thin films of the green mineral referred to below (symplesite).

The total water was determined by Penfield's method of direct weighing, and also by absorption. Some difficulty was at first experienced owing to the fact that the mineral, even when finely powdered, "spits" and flies about a lot on warming, and it further decomposes on heating more strongly, losing, in addition to water, a part or the whole of its arsenic which deposits on the cooler parts of the apparatus as transparent octahedra of As_2O_3.

Total water, by Penfield's method	17.57%
" " by absorption method...	20.28%

The latter is regarded as the more correct; in this determination a long tube was introduced between that containing the heated mineral and the absorption tube, and the water was drawn off from this by suction at a low temperature; the arsenious oxide which volatilised during the ignition was in this way deposited and left behind. The lower result by the Penfield method may be due to a slight loss, by evaporation, of the expelled water before weighing, and in any case the two determinations are not strictly comparable having been made on two different samples.

The amount of water lost at 100° C and at 110° C was obtained by noting the loss experienced by weighed amounts kept at these temperatures for two or three hours; and in one experiment by heating in a vacuum over phosphorus pentoxide on a water bath for 2½ hours till constant.

Loss after 5 hours on water bath in vacuo over P_2O_5	11.96%
" " heating for 2 hours at 100°C	10.52%
" " " " 2 " " 110°C	10.91%
" " " " 4 " " 160°C	11.66%

The fact that only about one half of the total water is driven off at 100°C, and that there is comparatively little further loss even after prolonged heating at 160°C, indicates that a part only of the water is loosely held as water of hydration. The remaining water is only expelled after intense ignition at such a temperature that the mineral suffers partial decomposition with disengagement of arsenious oxide; this second portion of water may be regarded as being present as water of constitution.

The results of the complete analyses are given in columns 1 and 2 below:—

	1.	2.	*Calculated.*
CaO	10.00	10.14	9.74
Fe_2O_3	35.72	36.81	37.10
As_2O_5	31.06	33.83	33.33
H_2O	20.28	20.28	19.83
	100.06	101.06	100.00

Water of hydration found 11.96%
" " " calculated 12.00%

As might be expected by analogy with other amorphous substances, the results obtained from the analyses do not lead exactly to any very simple formula for the mineral. The figures agree however in a general way with those calculated for $2Ca_3As_2O_8.3Fe_2^{III}As_2O_8.5Fe_2^{III}(OH)_6.23H_2O$ and given above in column 3. The percentage of water (corresponding to $23H_2O$) which should be lost, at 100° C, by a mineral having this composition is also in agreement with the loss actually observed on heating the substance to this temperature.

The substitution of $25H_2O$ for $23H_2O$ does not appreciably alter the figures, and the composition of such a mineral might be expressed by the general formula

$$(Ca_3,Fe_2^{III})As_2O_8.Fe_2^{III}(OH)_6.5H_2O, \text{ where } Ca_3: Fe_2^{III} = 2:3.$$

The mineral fuses readily, with intumescence, giving off white fumes of arsenious oxide and leaving a black magnetic globule. In the closed tube small fragments decrepitate violently and fly to pieces; water is first given off and at a higher temperature white arsenious oxide is deposited on the sides of the tube; when mixed with charcoal a black arsenical mirror is obtained instead.

The only well defined arsenates of iron and calcium at present known are *arseniosiderite*, $2Ca_3As_2O_8.Fe_2^{III}As_2O_8.3Fe_2^{III}(OH)_6$ and *mazapilite*, $Ca_3As_2O_8.Fe_2^{III}As_2O_8.Fe^{III}{}_2O_2(OH)_2$. The mineral described here can not be referred to either of these as regards its chemical composition, and it is further quite distinct from them in its physical characters. Neglecting the water of hydration, the composition is in a way comparable with that of arseniosiderite, the ratio of the total arsenate molecules to the ferric hydroxide being in each case 1:1. In the case of arseniosiderite, the ratio *calcium arsenate : ferric arsenate* as usually given in the text-books is 2 : 1. Published analyses however fail to support this, but show that the percentage of lime present is never high enough to conform to this theoretical ratio, the calcium and iron present in the form of arsenate, as actually found, being more nearly in the proportion Ca_3: $Fe^{'''}_2$ = 1 : 1, or even approaching 1 : 2. It would thus seem more in keeping with the facts to refer arseniosiderite to the general formula $(Ca_3,Fe^{'''}_2)As_2O_8.Fe^{'''}_2(OH)_6$. The Yukon mineral may then be expressed by the same general formula, with the addition of five molecules of water, and for such hydrous arsenates of iron and calcium the name *Yukonite* is proposed, in allusion to the locality in which the mineral now described is found.

It may be remarked that some *pitticite* (a hydrated ferric arsenate and sulphate of doubtful composition) closely resembles this mineral in colour, lustre and other physical characters.

The soft yellow ochreous material in which the mineral is embedded was not analysed quantitatively, but it contains the same constituents and has possibly been largely derived from its alteration; except for the fact that it is not fibrous, it might well be arseniosiderite. There is in addition a small amount of an apple or bluish-green mineral which occurs as minute rosettes of radiated fibres within the yellow substance, and also often forms a thin coating or film between the latter and the mineral described above. This could not be obtained in sufficient quantity for an analysis, but a qualitative test indicates that it is an arsenate. As seen under the microscope, the needles are strongly pleochroic, greenish-yellow for light vibrating along their length and bluish-green for transverse vibrations; between crossed nicols they usually show inclined extinction at angles up to 40°, and compensation takes place when the quartz wedge is inserted across their length. In all these characters, as well as in its general appearance and occurrence as fine radiated fibres, this mineral resembles *symplesite* ($Fe''_3As_2O_8.8H_2O$) and there can be no doubt that it is to be referred to this species. So far as the writer is aware, the occurrence of symplesite in North America has not been hitherto recorded.

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Note on the Occurrence of Scorodite, etc., at Cobalt, Northern Ontario, Canada.

By R. P. D. Graham.

A substance which resembles yukonite very closely in general appearance has recently been found by Mr. J. B. Tyrrell at Cobalt, Northern Ontario (Vein 49 of the Nipissing Mine).

This material has a coffee-brown colour, paler than yukonite, and is occasionally banded in different shades; like yukonite, also, it is amorphous, breaking with a conchoidal fracture, and the lustre is vitreous to resinous. H = 3 – 4; Sp. G. = 2.83.

Together with a paler yellow ochreous substance, it encrusts massive nickeliferous smaltite (or chloanthite), and there are also associated with it erythrite and on one of the specimens, a few minute crystals of scorodite. The erythrite, in the form of small botryoidal masses composed of radiated needles, is often seen forming a coating over the amorphous brown substance, and has probably been derived from its alteration.

The association with erythrite is interesting in view of the fact that yukonite is accompanied by symplesite (which is isomorphous with erythrite, containing iron in place of cobalt); and it was thought possible that the substance from Cobalt might be a Co-Ni compound analagous to yukonite, since the two materials are so much alike physically, and give rise to such nearly related decomposition products.

A preliminary examination showed that it is easily soluble in hydrochloric acid, and that it contains As, Fe, Co and Ni, but no Ca; there was no reaction for a sulphate or phosphate. When heated in a small blowpipe flame, it is easily fusible to a strongly magnetic mass, and in the closed tube it yields much acid water and a white deposit of arsenious oxide, the reaction taking place more readily when the substance has been previously mixed with charcoal powder.

In the analysis, the arsenic was precipitated as tri-sulphide from the reduced solution, dissolved and converted to magnesium pyroarsenate. The cobalt and nickel, after removal of the iron, were deposited electrolytically from an ammoniacal solution of their sulphates, and after the deposit had been weighed and dissolved, the cobalt was separated by precipitation with potassium nitrite, and both it and the nickel were then determined by precipitation with potash and bromine water. Owing to the small amount of material available, only one analysis, on 0·3392 grms., was made, and the water was estimated by difference.

	Found.	Calculated.
FeO	21·55	21·55
NiO	8·87	8·94
CoO	4·57	4·49
As_2O_5	41·09	41·31
H_2O (By diff.)	23·92	23·71

The figures obtained do not lead to any very simple formula, but agree in a general way with those calculated for $R''_3(AsO_4)_2.8H_2O$; this is the general formula for erythrite ($R'' = Co, Ni, Fe$) and also for forbesite ($R'' = Ni, Co, H_2$), the former being a normal arsenate, and the latter an acid salt, which is described as a substance of greyish-white colour and dull to silky or resinous lustre (Dana, 6th Ed. p. 834). The figures given in the second column above have been calculated for an acid arsenate of general composition $R''_3(AsO_4)_2.7H_2O$, where R'' is represented by (H_2, 5Fe, 2Ni, Co) in the proportions here given. This as nearly as possible represents the result of the analysis of the material, though there is no special reason for believing it to be an acid salt, related to forbesite, rather than a normal hydrous salt. The substance is mainly of interest as an unusual oxidation product of smaltite, and also from its physical resemblance to yukonite.

The associated scorodite is in the form of almost microscopic crystals not more than 0·2 m.m. in diameter; they were identified by measurement on the goniometer and by a determination of the specific gravity. This mineral has not been hitherto recorded from Canada.

The crystals are pale yellowish, transparent, with a very high lustre; in habit they are prismatic, terminated by pyramid faces, the only forms present being *d* { 120 } and *p* { 111 } a common combination with scorodite. The angles as measured are not identical with those usually given for scorodite, as the following axial ratios will show:

	a		*b*		*c*	Sp. G.
Scorodite...........	0·8658	:	1	:	0·9541	3·1—3·3
Crystals from Cobalt	0·8785	:	1	:	1·0555	3·235

Of these, the ratio *a* : *b* is probably about correct for the crystals, since the prism angle can be measured with fair accuracy and was observed on four crystals. The length of the vertical axis, *c*, is more doubtful, owing to the extremely small size of the pyramid faces.

It is possible that in these crystals, the iron may be in part replaced by cobalt, and this might account for the fact that the interfacial angles are not identical with those of normal scorodite. *Kobalt-scorodite* is reported by Lippmann as occurring at Schneeberg in bluish crystals which were not analysed (Dana, 6th Ed. p. 822). A borax bead test seemed to confirm the presence of cobalt in the crystals from Cobalt; but owing to the small amount of material used, and bearing in mind the fact that the associated minerals are all highly cobaltiferous, the result is considered doubtful.

The specific gravity was found to be 3·235, using methylene iodide and the Westphal balance.

The prism angle being nearly 60°, a rough measurement of the refractive index by the M.D. method was made, and gave a mean index of 1·76, with strong dispersion. There are apparently no published determinations of the refractive index of scorodite with which to compare this result.

The writer is indebted to Mr. J. B. Tyrrell for supplying the material described in the above note.

NOTE.—Since the above was written, Mr. Tyrrell has obtained some additional material from Cobalt, and the writer hopes to be able shortly to publish a fuller description of the brown amorphous substance described here.

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